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ON THE CORRELATION OF THE KINETICS OF ELECTRON TRANSFER PROCESS--ETC(U)
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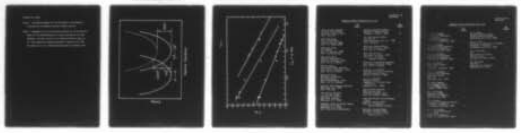

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by

Gary B. Schuster

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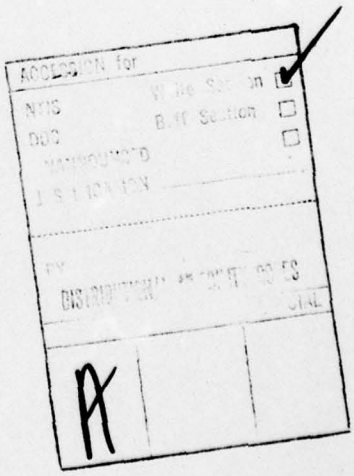
Abstract: The general electron transfer reaction mechanism proposed by Weller is analyzed for three specific cases: (i) the electron transfer is exergonic and irreversible, (ii) the electron transfer is endergonic and reversible, and (iii) the electron transfer is endergonic and irreversible. In the last case it is revealed that the correlation of the log of the overall reaction rate constant with reaction free energy gives a line with a slope of $-\alpha/RT$. The constant α is associated with the well-known transfer coefficient for electrode reactions. Analysis of the kinetics of chemically initiated electron-exchange luminescence (CIEEL) reactions reveals that they conform to the third case with α of ca. 0.3. Several other electron transfer reactions are suggested to be proceeding by this mechansim as well.



On the Correlation of the Kinetics of Electron Transfer Processes with the Change in Reaction Free Energy. Application to Electron-Exchange Initiated Chemiluminescence Reactions.

Sir:

Single electron transfer reactions to generate radical ion intermediates have been shown recently to be of crucial importance in the chemistry of organic and organometallic electronically excited states,[1] singlet oxygen,[2] radicals,[3] and organic peroxides.[4] The radical ions so produced have been observed to return to reactants (fluorescence quenching), to undergo further electron transfer reactions that lead eventually to products, to combine to generate products, and to annihilate to form electronically excited states (chemiluminescence). Often the evidence for the involvement of radical ion intermediates in these processes is a correlation of the observed rate constant for reaction with the one electron oxidation or reduction potential of the reactant.[5] Our recent work on chemically initiated electron-exchange luminescence (CIEEL) has produced several such correlations.[4e-4i] We report herein an interpretation of the kinetics of these apparently irreversible, endergonic, electron transfer reactions based upon the model proposed by Weller and coworkers.[6]

Equation 1 is an adapted version of the general reaction scheme presented by Rehm and Weller.[6b] The subscripts on the rate constants have been kept the same for consistency but the reactants have been generalized as donor (D) and acceptor (A) and the electronic states of these are left unspecified. The products (P) of the reaction may be different electronic states of the reactants or new substances.

$$D + A \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} D\text{----}A \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} {}^2D^{\cdot+}\text{----}{}^2A^{\cdot-} \xrightarrow{k_{30}} P \qquad (1)$$

The first equilibrium defines the diffusion of the reactants, the second the electron transfer process. It should be noted also that the final step (rate constant k_{30}) is irreversible and may correspond to diffusion apart of the ions or to chemical reaction. Application of the usual steady-state approximation to the concentration of encounter complex (D ---- A) and radical ion pair ($^2D^{\dot{+}}$ ---- $^2A^{\dot{-}}$) leads to equation 2 (analogous to Rehm and Weller[6b] equation 2) which defines the rate constant for formation of P (k_p). It is the correlation of this rate

$$k_p = \frac{k_{30}k_{23}k_{12}}{(k_{32} + k_{30})(k_{21} + k_{23})} \qquad (2)$$

constant with the energetics of the electron transfer ($\Delta G°$)[7] that can provide the kinetic evidence for an electron transfer in a reaction scheme. The relationship between the magnitude of the various rate constants of equation 2 apparently determine the nature of this correlation. Weller and coworkers,[6] for example, have observed diffusion limited electron transfer for which k_p is independent of $\Delta G°$ (case i, below) and endergonic electron transfer for which k_p depends strongly on $\Delta G°$ (case ii, below). Our observations[4e-4i] lead us to suggest a third general form for the correlation of k_p with $\Delta G°$ (case iii, below) which occurs when the electron transfer step is both endergonic and irreversible.

Case (i) The electron transfer step (k_{23}) is exergonic ($\Delta G°$=-) and irreversible.

The two conditions specified are not unrelated, the reverse electron transfer (k_{32}) must be endergonic and therefore activated. Diffusion of the radical ions or chemical reaction (k_{30}) could easily be orders of mag-

nitude more rapid.[8] Thus, $k_{32} << k_{30}$. If, as Weller reports, with these restrictions k_p is equal approximately to the diffusion limited rate constant k_{12}, then $k_{23} >> k_{21}$. In fact, this conclusion permits us to relax the stated requirement of irreversibility. When these inequalities are applied to equation 2 they lead to the conclusion that in this case there should be no correlation between $\Delta G°$ and k_p. The slope of a semilog plot of k_p against $\Delta G°$ should be equal to zero, as has been seen experimentally.[6a, b]

Case (ii) The electron transfer step k_{23} is endergonic ($\Delta G°=+$) and reversible.

As above, these two conditions are related. Back electron transfer (k_{32}) is now the exergonic direction and since exergonic electron transfer competes effectively with diffusion, $k_{32} >> k_{30}$. By analogy, $k_{23} << k_{21}$. That is, diffusion is faster than activated electron transfer. These inequalities applied to equation 2 lead to equation 3 where $K_{12} = k_{12}/k_{21}$ and $K_{23} = k_{23}/k_{32}$. Under these restrictions a semilog plot of k_p against $\Delta G°$ gives a line with a

$$k_p = k_{30}K_{12}K_{23} = k_{30}K_{12}e^{-\Delta G°/RT} \qquad (3)$$

slope of -1/RT. Observation of this behavior when $\Delta G°$ is represented as a linear function of the oxidation or reduction potential of the reactant has been taken as strong evidence for the involvement of a rate limiting electron transfer step on the reaction coordinate.[9] Moreover, this observation tends to support the postulate of the model that K_{12} is independent of $\Delta G°$. It should be noted that when $\Delta G° \sim 0$ the kinetics are apparently well fit by Weller's[6b] empirical equation and by Marcus' relationship.[10]

Case (iii) The electron transfer step (k_{23}) is endergonic ($\Delta G°$=+) and irreversible.

As above $k_{23} << k_{21}$ but now $k_{32} << k_{30}$ as well. Such a circumstance might be realized if gain (or loss) of an electron by the reactant generated a reactive radical ion that underwent irreversible chemistry at a rate faster than the back electron transfer. Substitution of the above inequalities into equation 2 leads to equation 4.

$$k_p = K_{12}k_{23} \tag{4}$$

Shown in figure 1 is an analysis of the relationship between k_{23} and $\Delta G°$. When $\Delta G°$=0 the activation barrier is $\Delta G_o^{\ddagger}$ (intersection of two solid curves) and has been associated with solvent reorganization.[10] If we now increase $\Delta G°$ for the electron transfer by increasing the oxidation potential of D by an amount $\Delta\Delta G°$, for example, the activation barrier for reaction also increases (intersection of solid and dotted curve) but not by the full amount $\Delta\Delta G°$. As a result of the geometry of the intersection only a fraction (α) of the total free energy change is realized as an increase in the activation barrier. The proportionality constant (α) is analogous to the well-known transfer coefficient and generally takes a value between 0.3 and 0.7 for electrode reactions.[11] We can therefore express k_{23} as a function of $\Delta G°$ according to equation 5 where k_i is the rate constant for reaction when $\Delta G° = 0$.

$$k_{23} = k_i e^{-\alpha\Delta G°/RT} \tag{5}$$

Substituting equation 5 into 4 leads to equation 6 which shows that under these conditions the slope of the semilog plot of k_p against $\Delta G°$ is $-\alpha/RT$.

$$k_p = K_{12}k_i e^{-\alpha\Delta G°/RT} \tag{6}$$

In the eventuality that K_{12} is somehow dependent on the value of ΔG° for the electron transfer reaction then the measured value of α is a composite of the transfer coefficients for the encounter complex and for the electron transfer.

Our investigation of the CIEEL mechanism for various peroxides[4e-4i] has revealed the correlation of the rate constant of the chemiluminescent reaction with the activator oxidation potential shown in Figure 2. These data are apparently consistent with the third case of the above model. We associate k_{30} with the irreversible cleavage of the oxygen-oxygen bond of the reduced peroxide. For these reactions α apparently takes a value of ca. 0.3.

A survey of the recent literature reveals that the kinetic behavior predicted by the requirements of Case iii might be quite often observed. For example, Chan and Bruice[12] have investigated the reaction of nitroxides with 1,5-dihydroflavins and $N^{3,5}$-dimethyl-1,5-dihydrolumiflavin. Their findings indicate a one electron-transfer process. Analysis of their data indicate that they are consistent also with the third case identified above with $\alpha = 0.32$. For this system k_{30} can be associated with proton transfer from the oxidized flavin to the reduced nitroxide. Thomas and Foote[2c] have reported on an apparent electron transfer reaction from substituted phenols to singlet oxygen that is consistent with the third case outlined above. For this reaction, k_{30} may be associated with the formation of a carbon-oxygen bond or transfer of a proton from phenol radical cation to superoxide radical anion and $\alpha = 0.44$. Bank and Juckett[13] have seen a similar correlation in a study of the reaction of sodium naphthalide with alkyl halides. In this case $\alpha = 0.23$ and k_{30} might correspond to the cleavage of the carbon-halogen bond.[14]

Also, Gardner and Kochi[15] have observed a dependence of the rate of oxidation of tetraalkyl lead compounds with hexachloroiridate (IV) that appears to be consistent with the model for endergonic irreversible electron transfer.[14] For this reaction we would associate k_{30} with the cleavage of the lead carbon bond and $\alpha = 0.39$.

In summary, we have presented an analysis of electron transfer reactions that leads to the prediction of three limiting forms for the correlation of kinetics and energetics. Each of these forms has been observed experimentally. We are continuing our investigation of endergonic irreversible electron transfer reactions.

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7. ΔG° is the free energy change for the net electron transfer for reaction and has been equated to solution phase oxidation and reduction potentials and dipolar coulombic attraction.[6a,b,10] $\Delta G^\circ = E(D/D^+) - E(A^-/A) - \frac{e^2}{\varepsilon r}$ where $E(D/D^+)$ is the oxidation potential of the donor, $E(A^-/A)$ the reduction potential of the acceptor, e is the electronic charge, ε the dielectric constant of the medium and r the distance between the ions.

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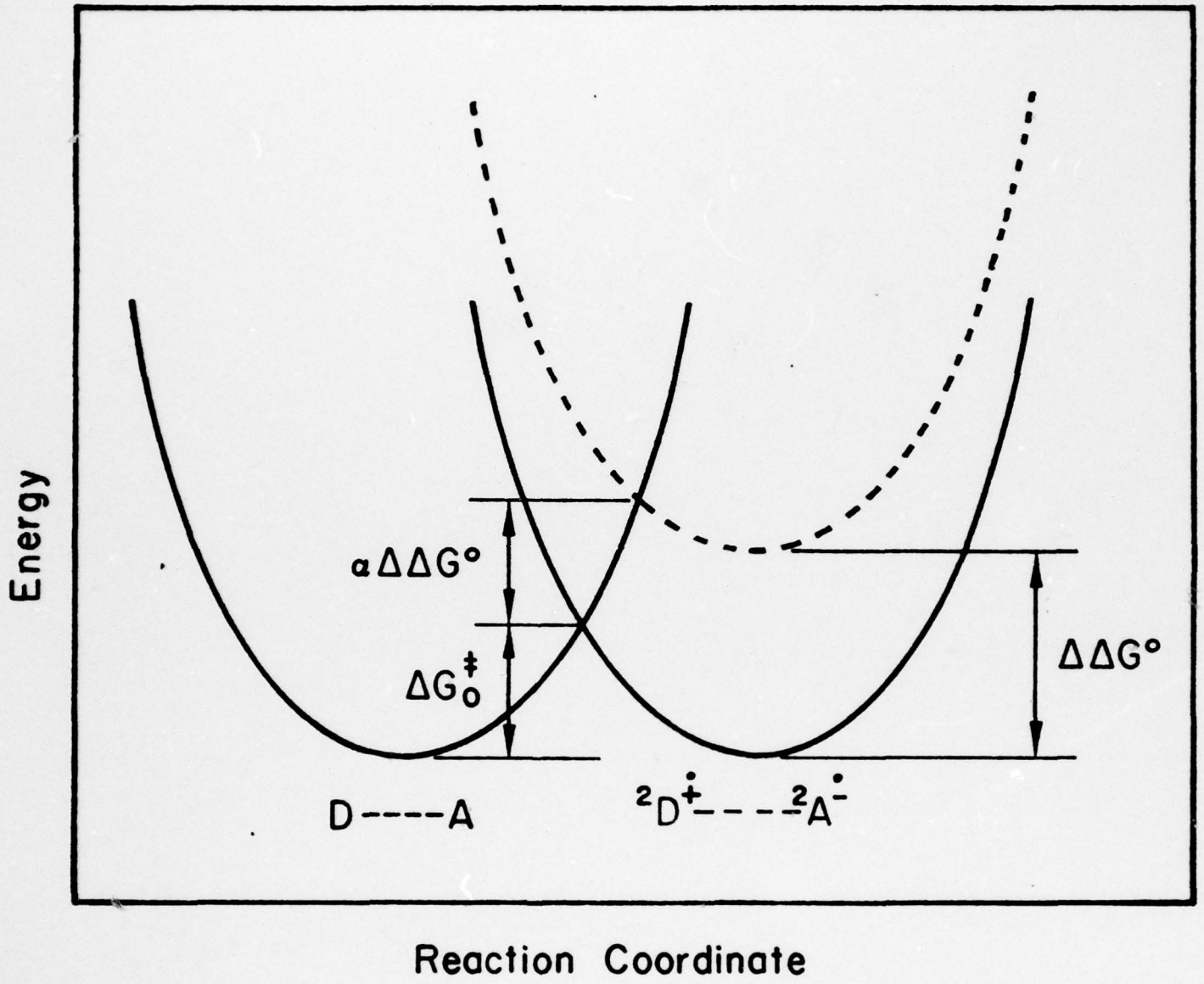
Captions for Figures

Figure 1. Relationship between $\Delta\Delta G^\circ$ and the change in free energy of activation for an endergonic electron transfer reaction.

Figure 2. Dependence of k_p on the oxidation potential of various electron donors for the chemiluminescence of organic peroxides by the CIEEL mechanism. The open circles are for diphenoylperoxide in CH_2Cl_2 at 27°, the triangles for dimethyldioxetanone in benzene at 24°, and the closed circles for 1-phenylethylperoxyacetate in benzene at 99°.


Energy
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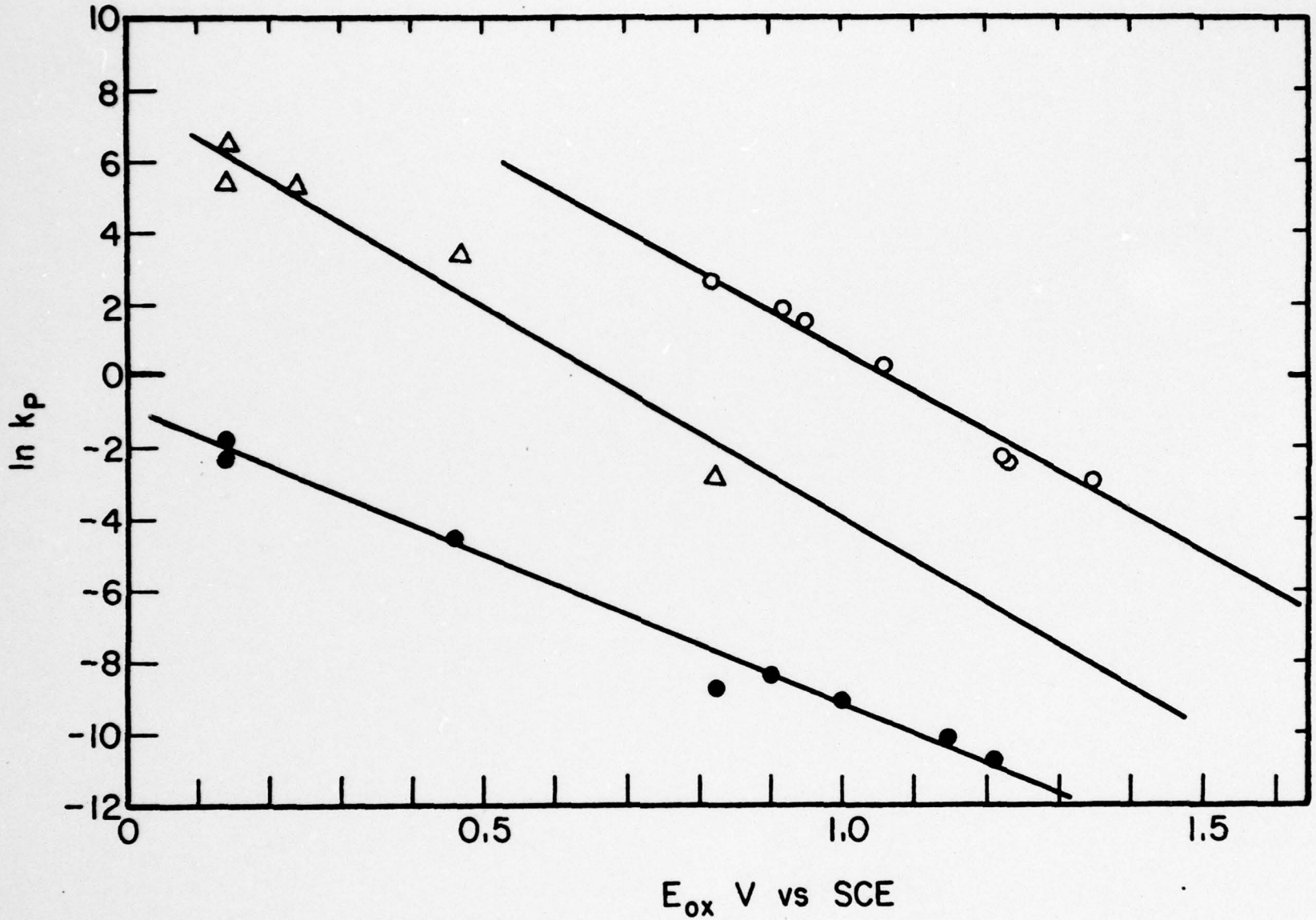
ΔG‡o
ΔΔG°
D----A
2D+---2A-
Reaction Coordinate

Figure 2



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